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14. ABSTRACT

Our goal was to develop novel multiparticle computational tools for materials science based on representing operators and functions of many variables as short sums of separable functions. We have extended multiresolution separated representation of free-space Green's functions to those periodic or satisfying boundary conditions, making fast algorithms available for solving integral equations.

The problem of incorporating inter-electron cusps led us to the problem of approximating multivariable functions by sums of products of Gaussians, for which we developed and tested a new (suboptimal) algorithm. For optimal representations, we have developed an algorithm in the case of two variables; extensions to higher dimensions need further work. We also constructed novel separated representations of non-convolutional Green's functions and spectral projectors for operators with potentials from the Rollnik class which include all physically significant potentials considered within a finite domain.

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We started work on implementations
of these algoritrhms in the Python environment in order to use them for practical computations.

We have developed the algorithmic framework for a size-extensive/consistent method for the multiparticle Schrodinger equation. The central computation involved has revealed a center-of-mass principle for electrons, which gives hope for the construction of an analogue of the Fast Multipole Method for quantum mechanical systems.

FINAL REPORT "SEPARATED REPRESENTATIONS FOR COMPUTATIONAL MATERIALS SCIENCE" AWARD W911NF-04-1-0281 PERIOD: JULY 1, 2004 TO OCTOBER 31, 2005

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1. Abstract

Our goal was to develop novel multiparticle computational tools for materials science based on representing operators and functions of many variables as short sums of separable functions.

We have extended multiresolution separated representation of free-space Green's functions to those periodic or satisfying boundary conditions, making fast algorithms available for solving integral equations.

The problem of incorporating inter-electron cusps within two-particle methods led us to the problem of approximating multivariable functions by sums of products of Gaussians. We have developed and tested a new (suboptimal) algorithm, sufficient for many practical purposes. Using this algorithm we constructed novel separated representations of non-convolutional Green's functions and spectral projectors for operators with potentials from the Rollnik class. Such potentials include all physically significant potentials considered within a finite domain. For optimal representations, we have developed an algorithm in the case of two variables; extensions to higher dimensions need to be worked on further. We started work on moving preliminary implementations of these algoritrhms into the Python environment where they can be used for practical computations.

We have developed the algorithmic framework for a size-extensive/consistent method for the multiparticle Schrodinger equation. The central computation involved has revealed a center-of-mass principle for electrons, which gives hope for the construction of an analogue of the Fast Multipole Method for quantum mechanical systems.

2. Tasks

Our work addresses three tasks in using separated representations [11, 9] for computational materials science. In our proposal we organized these tasks by increasing degree of difficulty. They are:

1. Incorporating multiresolution separated representations into existing methods in materials science (where the underlying dimension is three) and, thus, simplifying computations involving Green's functions with boundary conditions (or periodic)
2. "Upgrading" computational chemistry from one-particle theories to using two-particle theories (with underlying dimension six).

3. Developing methods for solving the multiparticle Schrödinger equation of quantum mechanics, where the dimension grows linearly with the number of particles. In particular, our goal is finding computational methods that incorporate algorithmic size-extensivity.

3. Results for Task 1: Multiresolution separated representations of Green's functions with boundary conditions

Our goal has been to obtain multiresolution representations of lattice sums for Green's functions (as well as potentials) in a form that facilitates solving integral equations. We note that computations involving multidimensional free space Green's functions are greatly simplified by using separated representations [11, 9, 28, 30, 50, 51, 22, 8]. Using lattice sums, we have constructed separated representations of Green's functions with periodic, Dirichlet or Neumann boundary conditions. Such lattice sums are not absolutely convergent and we have developed an explicit multiresolution interpretation of these sums.

Our approach is based on representing spherically symmetric functions by sums of products of Gaussians. Such approximations are obtained by discretizing integrals which are similar, or even identical, to those used in the Ewald summation. However, even though conceptually our construction has strong similarities with the Ewald summation, it differs in important details. We compute separated representations of lattice sums using only one dimensional integrals or sums. The resulting approximation is a combinations of three terms, a smooth periodic term with a short Fourier expansion, and two terms, a singular and non-singular, the sum of which is near zero outside the ball inscribed into a unit cell (for any finite but arbitrary accuracy). The number of terms needed in the final representation is (nearly) optimal.

3.1. **Technical Introduction: separated representations of lattice sums.**

A practical way of computing Green's functions and periodic potentials via lattice sums has been of interest for many years. An early seminal contribution was made by P. Ewald [21], although the history of lattice sums starts earlier and we refer to [25] for a historical overview and results prior to 1980. A more recent fundamental advance was made in [32], where a surprisingly simple integral representations of harmonic lattice sums has been derived.

Our goal is to compute representations of lattice sums for Green's functions and potentials in a form that facilitates solving integral equations. We note that computations involving multidimensional free space Green's functions are greatly simplified by using separated representations [9, 10, 28, 30, 50, 51, 22, 8]. Using the lattice sums, we construct separated representations of Green's functions with periodic or zero boundary conditions. Such lattice sums are not absolutely convergent and we develop an explicit multiresolution interpretation of these sums. We note that we selected the Green's functions for the Poisson and the bound state Helmholtz operators as examples since the same method applies equally well to other non-oscillatory Green's functions.

For spherically symmetric singular potentials it has been traditional to rely on spherical harmonics as a tool for computing lattice sums. The essential difficulty in such approach is to combine together local spherical symmetry and summation over directional shifts. In our approach we avoid this difficulty by representing spherically symmetric functions in the Cartesian system of coordinates by using

sums of products of Gaussians. Such separated representations are constructed to be accurate over a remarkably wide range of spatial scales since the number of terms grows only as $\mathcal{O}(-\log(\delta))$, where δ is the distance away from the singularity. The summation over directional shifts then proceeds in the term by term fashion and involves sums only over one-dimensional lattices.

3.2. **Preliminary Considerations.**

3.2.1. *Separated representations for Poisson-type kernels.* Let us construct a separated approximation of the function $1/r^\alpha$, where $r = ||\mathbf{x}||$, $\mathbf{x} \in \mathbb{R}^3$ using a collection of Gaussians. The approximation is obtained by first discretizing the integral

$$\frac{1}{r^\alpha} = \frac{2}{\Gamma(\alpha/2)} \int_{-\infty}^{\infty} e^{-r^2 e^{2s} + \alpha s}\, ds\,. \tag{3.1}$$

For $\alpha = 1$ it is the same integral as used in the Ewald summation (up to a change of variables, see e.g., [25]). We have

Proposition 3.1. *For any $\alpha > 0$, $0 < \delta \le 1$, and $0 < \epsilon \le \min\left\{\frac{1}{2}, \frac{\delta}{\alpha}\right\}$, there exist positive numbers p_m and w_m such that*

$$\left| \frac{1}{r^\alpha} - \sum_{m=1}^{M} w_m e^{-p_m r^2} \right| \le \frac{\epsilon}{r^\alpha}, \tag{3.2}$$

where

$$M = \log \epsilon^{-1} [c_0 + c_1 \log \epsilon^{-1} + c_2 \log \delta^{-1}], \tag{3.3}$$

where c_1, c_2 and c_3 are constants that only depend on α. For fixed power α and accuracy ϵ, we have $M = \mathcal{O}(\log \delta^{-1})$.

A proof of Proposition 3.1 can be found in [13].

Using $r = ||x||$, where $x = (x_1, x_2, x_3)$, and $\alpha = 1$ in (3.2), we arrive at a separated representation for the Poisson kernel. Although in this paper we compute the lattice sums corresponding to the Poisson kernel, the same approach will work for any $\alpha > 0$ as well as other spherically symmetric potentials, e.g. Yukawa potential $e^{-\mu r}/r$.

As in [28, 30], the approximation in (3.2) is obtained using trapezoidal rule. First, we discretize the integral (3.1), namely, set $p_m = e^{2s_m}$ and $w_m = 2\Delta s\, e^{\alpha s_m}/\Gamma(\alpha/2)$, where $s_m = s_0 + (m-1)\Delta s$, $m = 1 \ldots, M$. For a given accuracy ϵ and range $0 < \delta \le r \le 1$, we select s_0 and $s_M = s_0 + (M-1)\Delta s$, the end points of the interval of integration replacing the real line in (3.1), so that at these points the function $f(s) = e^{-r^2 e^{2s} + \alpha s}$ and a sufficient number of its derivatives are close to zero to within the desired accuracy. We also select M, the number of points in the quadrature, so that the accuracy requirement is satisfied.

3.2.2. *The cross-correlation functions.* We use the scaling functions of the multiwavelet bases developed in [2]. For a brief review of the multiwavelet bases see also [3]. For convolution operators we only need to compute integrals with the cross-correlation functions of the scaling functions, namely,

$$\Phi_{ii'}(x) = \begin{cases} \Phi^{+}_{ii'}(x), & 0 \le x \le 1, \\ \Phi^{-}_{ii'}(x), & -1 \le x < 0, \\ 0, & 1 < |x|, \end{cases} \tag{3.4}$$

where $i, i' = 0, \ldots, \mathfrak{m}-1$, $\mathfrak{m}$ is the order of the basis, and

$$\Phi^+_{ii'}(x) = \int_0^{1-x} \phi_i(x+y)\,\phi_{i'}(y)dy\,, \quad \Phi^-_{ii'}(x) = \int_{-x}^{0} \phi_i(x+y)\,\phi_{i'}(y)dy\,. \tag{3.5}$$

The scaling functions ϕ_i are the normalized Legendre polynomials on the interval $[0,1]$,

$$\phi_i(x) = \begin{cases} \sqrt{2i+1}P_i(2x-1), & x \in [0,1] \\ 0, & x \notin [0,1] \end{cases},$$

where P_i are the Legendre polynomials on $[-1,1]$. This implies that the functions $\Phi_{ii'}$ are piecewise polynomials of degree $i+i'+1$ with the support in $[-1,1]$.

Proposition 3.2.

1. *Transposition of indices:* $\Phi_{ii'}(x) = (-1)^{i+i'}\Phi_{i'i}(x)$,
2. *Relations between* Φ^+ *and* Φ^-*:* $\Phi^-_{i,i'}(-x) = (-1)^{i+i'}\Phi^+_{i,i'}(x)$ *for* $0 \le x \le 1$,
3. *Values at zero:* $\Phi_{ii'}(0) = 0$ *if* $i \neq i'$, *and* $\Phi_{ii}(0) = 1$ *for* $i = 0, \ldots, \mathfrak{m}-1$,
4. *Upper bound:* $\max_{x\in[-1,1]} |\Phi_{ii'}(x)| \le 1$ *for* $i, i' = 0, \ldots, \mathfrak{m}-1$,
5. *Connection with the Gegenbauer polynomials:* $\Phi^+_{00}(x) = \frac{1}{2}\,C_1^{(-1/2)}(2x-1) + \frac{1}{2}$ *and* $\Phi^+_{l0}(x) = \frac{1}{2}\,\sqrt{2l+1}\,C_{l+1}^{(-1/2)}(2x-1)$, *for* $l = 1, 2, \ldots$, *where* $C_{l+1}^{(-1/2)}$ *is the Gegenbauer polynomial,*
6. *Linear expansion:* $\Phi^+_{ii'}(x)$ *are linear combinations*

$$\Phi^+_{ii'}(x) = \sum_{l=i'-i}^{i'+i} c^l_{ii'}\Phi^+_{l0}(x), \tag{3.6}$$

where

$$c^l_{ii'} = \int_0^1 \Phi^+_{ii'}(x)\Phi^+_{l0}(x)(1-x^2)^{-1}dx. \tag{3.7}$$

7. *Vanishing moments: we have* $\int_{-1}^1 \Phi_{00}(x)\,dx = 1$ *and* $\int_{-1}^1 x^k\Phi_{ii'}(x)\,dx = 0$ *for* $i + i' \ge 1$ *and* $0 \le k \le i + i' - 1$.

3.3. **Multiresolution representation of lattice sums.** Since the sum in (3.14) is not absolutely convergent, we need to provide its interpretation. Our derivation in previous sections used the usual justification for Ewald summation, see e.g. [25]. In this section we interpret the divergent sum in (3.14) using multiresolution representation of the Poisson kernel as a starting point. This allows us to obtain simple and transparent conditions for the shape of the domain over which the summation is performed as well as to observe that the complexity of the algorithm to apply the periodic Green's function is the same as that for the Green's function in $\mathbb{R}^3$ where the differences between the two occurs only on coarse scales.

Let us begin with the multiresolution representation of the Poisson kernel in $\mathbb{R}^3$. We use multiwavelet bases [2] as we find them more appropriate for numerical applications [3], [30] although other wavelet bases may be used in this construction

as well. The multiwavelet bases are constructed in $L^2(B)$, $B = [-1/2, 1/2]^3$and then extended to form a basis in $L^2(\mathbb{R}^3)$ by replicating the construction for each cube shifted by $\mathbf{n} \in \mathbb{Z}^3$ (see e.g. [3]). Let $V_j \in L^2(\mathbb{R}^3)$ denote subspaces of the multiresolution analysis corresponding to a multiwavelet basis of order $\mathfrak{m}$, where $\mathfrak{m}$ is the number of nodes in the Gaussian quadrature (in each direction). We then have

$$V_0 \subset V_1 \subset V_2 \subset \cdots \subset V_j \cdots$$

or, for each V_n,

$$V_n = V_0 \oplus W_0 \oplus W_1 \oplus \cdots \oplus W_{n-1}$$

where $V_j \oplus W_j = V_{j+1}$. The subspace V_0 is spanned by products of orthogonal polynomials up to degree $\mathfrak{m} - 1$ in each variable localized within cubes shifted by $\mathbf{n} \in \mathbb{Z}^3$.

Let P_j and Q_j denote the orthogonal projectors on spaces V_j and W_j, respectively. Given an operator T, we obtain its telescopic series as

$$T = T_0 + (T_1 - T_0) + (T_2 - T_1) + \ldots,$$

where $T_j = P_j T P_j$ is the projection of the operator T on the subspace V_j. It is easy to see that

$$T_{j+1} - T_j = Q_j T Q_j + Q_j T P_j + P_j T Q_j,$$

is the element of the non-standard form of the operator T on the scale j [6]. It was shown in [6] that the vanishing moments of the wavelet basis (this property remains unchanged for multiwavelets) yield a rapid decay of the coefficients of $T_{j+1} - T_j$ away from the singularity of the kernel. The rate of decay is controlled by the number of the vanishing moments which we choose depending on the accuracy requirement as will be explained below. By choosing $\mathfrak{m} > 2$, we assure the rate of decay of at least $1/r^{\mathfrak{m}+1}$ for all terms in the telescopic series except for T_0. If we now sum over the periodic lattice, separately on each scale, the sum is rapidly convergent for all terms except that for T_0. In fact, by selecting the number of vanishing moments of the basis, we control the rate of decay and may choose that number so that for a fixed but arbitrary precision the contribution of all outside terms is negligible.

What remains to be shown is how to perform the summation on V_0, making it the key to the multiresolution definition of the periodic Green's function. The projection T_0 of the Poisson kernel is given by the integrals

$$t^{\mathbf{n}}_{ii',jj',kk'} = \int_B \frac{1}{||\mathbf{x} + \mathbf{n}||} \Phi_{ii'}(x_1)\, \Phi_{jj'}(x_2)\, \Phi_{kk'}(x_3)\, d\mathbf{x}\,, \tag{3.8}$$

where $\mathbf{n} \in \mathbb{Z}^3$, $B = [-1/2, 1/2]^3$, $\mathbf{x} = (x_1, x_2, x_3)$, $i, i', j, j', k, k' = 0, \ldots, \mathfrak{m} - 1$ and $\mathfrak{m}$ is the order of the basis (the number of nodes in the Gaussian quadrature). We now need to interpret

$$t^{per}_{ii',jj',kk'} = \sum_{\mathbf{n} \in \mathbb{Z}^3} t^{\mathbf{n}}_{ii',jj',kk'} = \sum_{\mathbf{n} \in \mathbb{Z}^3} \int_B \frac{1}{||\mathbf{x} + \mathbf{n}||} \Phi_{ii'}(x_1)\, \Phi_{jj'}(x_2)\, \Phi_{kk'}(x_3)\, d\mathbf{x}\,, \tag{3.9}$$

integrals with cross-correlation functions rather than the sum in (3.14).

Let us consider $t^{\mathbf{n}}_{ii',jj',kk'}$ as a function of $\mathbf{n} \in \mathbb{Z}^3$. Using

$$\frac{1}{||\mathbf{x}+\mathbf{n}||} = \frac{1}{||\mathbf{n}||} - \frac{\mathbf{x}\cdot\mathbf{n}}{||\mathbf{n}||^3} - \frac{1}{2}\frac{||\mathbf{x}||^2}{||\mathbf{n}||^3} + \frac{3}{2}\frac{(\mathbf{x}\cdot\mathbf{n})^2}{||\mathbf{n}||^5} + \mathcal{O}(\frac{1}{||\mathbf{n}||^4}), \tag{3.10}$$

we observe that the coefficient $t^{per}_{00,00,00}$ cannot be given any meaning through the sum in (3.9). However, if we apply the resulting operator to periodic functions with zero mean, then the coefficient $t^{per}_{00,00,00}$ is not needed and we simply set $t^{per}_{00,00,00} = 0$ rather than use (3.9).

For $i + i' \geq 1$ all functions $\Phi_{ii'}$ (see Section 3.2.2) have vanishing moments, namely,

$$\int_{-1}^{1} \Phi_{ii'}(x)\, x^m\, dx = 0, \quad 0 \leq m \leq i + i' - 1. \tag{3.11}$$

Using (3.11) and (3.10), integrals (3.9) involving functions any function $\Phi_{ii'}$ with indices $i + i' \geq 3$ result in a rapid decay of the coefficients $t^{\mathbf{n}}_{ii',jj',kk'} = \mathcal{O}(\frac{1}{||\mathbf{n}||^4})$ and, therefore, the corresponding sum in (3.9) will converge absolutely.

Let us now examine integrals (3.9) involving function $\Phi_{ii'}$ with indices $1 \leq i+i' \leq 2$. We find that not all slowly decaying terms in (3.10) vanish. For example, using (3.9) and (3.10), and the fact that Φ_{01} is an odd function, we have

$$I_{01,00,00}(\mathbf{n}) = \frac{n_1}{||\mathbf{n}||^3} \left(\int_{-1}^{1} x\, \Phi_{01}(x)dx\right) \left(\int_{-1}^{1} \Phi_{00}(x)dx\right)^2 + \mathcal{O}(\frac{1}{||\mathbf{n}||^4}), \tag{3.12}$$

and, using the fact that Φ_{11} is an even function,

$$I_{11,00,00}(\mathbf{n}) = \frac{2n_1^2 - n_2^2 - n_3^2}{2||\mathbf{n}||^5} \left(\int_{-1}^{1} x^2\, \Phi_{11}(x)dx\right) \left(\int_{-1}^{1} \Phi_{00}(x)dx\right)^2 + \mathcal{O}(\frac{1}{||\mathbf{n}||^4}). \tag{3.13}$$

In all of these cases (conditional) summation over symmetric ranges of indices cancels the first term and yields convergent sums for the coefficients $t^{per}_{ii',jj',kk'}$, thus completing the multiresolution definition of the periodic Green's function.

3.4. **Lattice sums for 3D cubic lattice.** Let us now describe how to use (3.2) in a more traditional approach to lattice sums. Let us consider the cubic lattice (with some modifications the results can be extended to a general lattice). Starting with the free space Poisson kernel (or, alternatively, the Coulomb potential), let us compute for $\mathbf{x} \in B$,

$$G_0(\mathbf{x}) = \sum_{\mathbf{n}\in\mathbb{Z}^3} \frac{1}{||\mathbf{x}+\mathbf{n}||} = \frac{1}{||\mathbf{x}||} + \sum_{\mathbf{n}\in\mathbb{Z}^3}{}' \frac{1}{||\mathbf{x}+\mathbf{n}||}, \tag{3.14}$$

where the unit cell $B = [-1/2, 1/2]^3$. Formally G_0 is the Green's function in B,

$$-\nabla^2 G_0(\mathbf{x}) = 4\pi\delta(\mathbf{x}),$$

with the periodic boundary conditions. Since the sum (3.14) is not absolutely convergent, summation in (3.14) needs a separate description. If we apply the Green's function G_0 only to periodic functions integrating to zero in B, $\int_B f(\mathbf{x})d\mathbf{x} = 0$, then (3.14) is a conditionally convergent sum. Let us first assume that the convergence issues are resolved via a procedure described in e.g. [25] or via a multiresolution justification of such summation in Section 3.3.

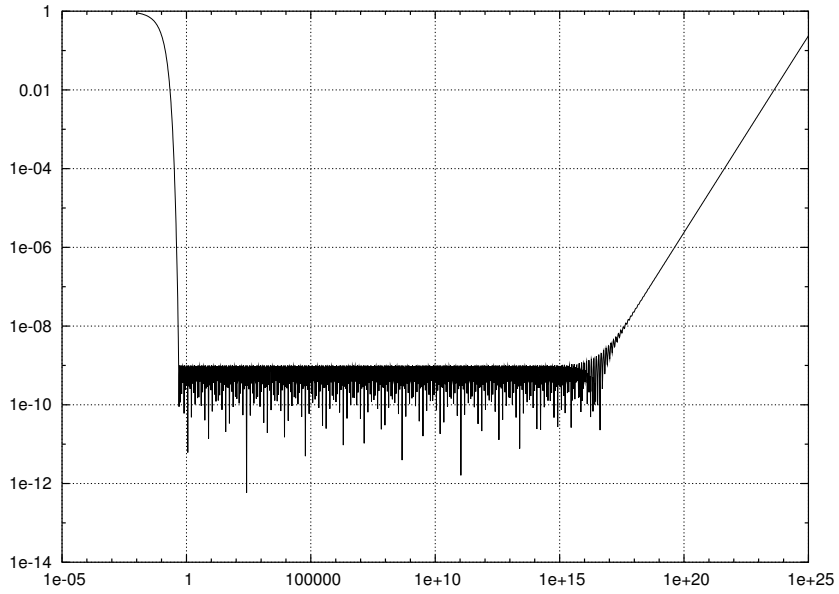


FIGURE 3.1. Relative error ($\log_{10}$) of approximating the Poisson kernel in (3.15), where $\epsilon = 10^{-9}$, $1/2 \leq ||x|| \leq 10^{15}$.

Let $r_0 = 1/2$ be the radius of the ball inscribed into B . We rescale (3.2) to approximate $1/r$ *outside* the ball B, in the region $r \in [r_0, R]$, where R is a large number. We obtain for $1/2 \leq r \leq 1/(2\delta)$,

$$|\frac{1}{r} - \sum_{m=1}^{M} \rho_m e^{-t_m r^2}| \leq \frac{\epsilon}{r}, \tag{3.15}$$

where $t_m = 4p_m\delta^2$ and $\rho_m = 2w_m\delta$. The error $\epsilon(r) = r|\frac{1}{r} - \sum_{m=1}^{M} \rho_m e^{-t_m r^2}|$ is illustrated in Figure 3.1. In this case $M = 270$, $t_m = e^{2\tau_m}$ and $\rho_m = \sigma \cdot e^{\tau_m}$, where $\tau_0 = -59.004022799786696$, $\Delta = 0.22676579925650819$, $\sigma = 0.25587780369080371$, and $\tau_m = \tau_0 + \Delta(m-1)$ with $m = 1, \ldots M$. As it turns out, we need only some of these terms and we let the algorithm select the necessary ones. We note that in this example the largest exponent in (3.15) is ≈ 54.

Assuming that we assign the lattice sum Σ' a finite value following, for example, the recipe in [25], we have formally

$$|\sum_{\mathbf{n}\in\mathbb{Z}^3}{}' \frac{1}{||\mathbf{x}+\mathbf{n}||} - \sum\nolimits_{m=1}^{M} \rho_m \sum_{\mathbf{n}\in\mathbb{Z}^3}{}' e^{-t_m||\mathbf{x}+\mathbf{n}||^2}|| \leq \epsilon \sum_{\mathbf{n}\in\mathbb{Z}^3}{}' \frac{1}{||\mathbf{x}+\mathbf{n}||}\,. \tag{3.16}$$

Using (3.14) and (3.16), we obtain an approximation to G_0 as

$$G_0^{appr}(\mathbf{x}) = \frac{1}{||\mathbf{x}||} - \sum_{m=1}^{M} \rho_m e^{-t_m||\mathbf{x}||^2} + G_0^{per}(\mathbf{x}),$$

where G_0^{per} is the periodic component,

$$G_0^{per}(\mathbf{x}) = \sum_{m=1}^{M} \rho_m \sum_{\mathbf{n}\in\mathbb{Z}^3} e^{-t_m||\mathbf{x}+\mathbf{n}||^2}. \tag{3.17}$$

By construction, for $\mathbf{x} \in B$ the combination

$$\frac{1}{||\mathbf{x}||} - \sum_{m=1}^{M} \rho_m e^{-t_m||\mathbf{x}||^2}, \tag{3.18}$$

is less than ϵ outside of the ball of radius $1/2$. Evaluating the sum in (3.18) only for $\mathbf{x} \in B$, we significantly reduce the necessary number of terms, since within accuracy ϵ contributions of many terms in (3.15) are accounted for by a constant.

Next let us compute the Fourier coefficients of the periodic function G_0^{per}. We have for $\mathbf{p} \in \mathbb{Z}^3$,

$$\hat{g}_{\mathbf{p}} = \int_B (\sum_{m=1}^{M} \rho_m \sum_{\mathbf{n}\in\mathbb{Z}^3} e^{-t_m||\mathbf{x}+\mathbf{n}||^2})\, e^{-2\pi i \mathbf{x}\cdot\mathbf{p}} d\mathbf{x} = \sum_{m=1}^{M} \rho_m \int_{\mathbb{R}^3} e^{-t_m||\mathbf{x}||^2}\, e^{-2\pi i \mathbf{x}\cdot\mathbf{p}} d\mathbf{x},$$

and, therefore,

$$\hat{g}_{\mathbf{p}} = \pi^{3/2} \sum_{m=1}^{M} \frac{\rho_m}{t_m^{3/2}}\, e^{-\pi^2\mathbf{p}^2/t_m}. \tag{3.19}$$

The coefficient $\hat{g}_{\mathbf{0}}$ is not well-defined by (3.19), since as we improve the approximation (3.15), the expression (3.19) diverges. However, we only apply G_0 to periodic functions with zero mean; thus, we define G_0^{per} using (3.19) for $\mathbf{p} \neq \mathbf{0}$ and set $\hat{g}_{\mathbf{0}} = \mathbf{0}$. The Fourier coefficients decay rapidly and we arrive at the separated representation,

$$G_0^{per}(\mathbf{x}) = \sum_{m=1}^{M} \rho_m \sum_{\mathbf{p}\in\mathbb{Z}^3,\, \mathbf{p}\neq\mathbf{0}} \frac{\pi^{3/2}}{t_m^{3/2}}\, e^{-\pi^2\mathbf{p}^2/t_m} e^{2\pi i \mathbf{x}\cdot\mathbf{p}}. \tag{3.20}$$

In (3.20) let us find $\hat{M} \leq M$ such that

$$\sum_{m=\hat{M}+1}^{M} \rho_m \frac{\pi^{3/2}}{t_m^{3/2}}\, e^{-\pi^2/t_m} \leq \epsilon.$$

We then have

$$G_0^{per}(\mathbf{x}) = \sum_{m=1}^{\hat{M}} \rho_m \sum_{\mathbf{p}\in\mathbb{Z}^3} \frac{\pi^{3/2}}{t_m^{3/2}}\, e^{-\pi^2\mathbf{p}^2/t_m} e^{2\pi i \mathbf{x}\cdot\mathbf{p}} - \sum_{m=1}^{\hat{M}} \rho_m \frac{\pi^{3/2}}{t_m^{3/2}}\,. \tag{3.21}$$

3.5. **Computing of Madelung Potentials.** Let us consider potential defined by the lattice sum

$$G_M(\mathbf{x}) = \sum_{\mathbf{n}\in\mathbb{Z}^3} \frac{(-1)^{n_1+n_2+n_3}}{||\mathbf{x}+\mathbf{n}||} = \frac{1}{||\mathbf{x}||} + \sum_{\mathbf{n}\in\mathbb{Z}^3}{}' \frac{(-1)^{n_1+n_2+n_3}}{||\mathbf{x}+\mathbf{n}||}, \tag{3.22}$$

describing the crystal lattice of *NaCl*. The function $G_M(\mathbf{x})$ is also the Green's function

$$-\nabla^2 G_M(\mathbf{x}) = 4\pi\delta(\mathbf{x}),$$

in $B = [-1/2, 1/2]^3$ with the zero boundary conditions. The second term in (3.22) evaluated at zero is the Madelung constant,

$$\mu = \sum_{\mathbf{n}\in\mathbb{Z}^3}{}' \frac{(-1)^{n_1+n_2+n_3}}{||\mathbf{n}||}.$$

A careful computation of the value of Madelung constant $\mu = -1.74756459...$ can be found in e.g. [15], and this potential and the constant have been computed by a variety of methods [25] making it easy to compare with our approach. We have from (3.15) and (3.16) an approximation

(3.23)

$$G_M^{appr}(\mathbf{x}) = \frac{1}{||\mathbf{x}||} - \sum_{m=1}^{M} \rho_m\, e^{-t_m||\mathbf{x}||^2} + \sum_{m=1}^{M} \rho_m\, Q(t_m, x_1)Q(t_m, x_2)Q(t_m, x_3),$$

where

$$Q(\tau, x) = \sum_{n\in\mathbb{Z}} (-1)^n\, e^{-\tau(x+n)^2} = \sum_{n\in\mathbb{Z}} (e^{-4\tau(x/2+n)^2} - e^{-4\tau(x/2+n+1/2)^2}).$$

For the Madelung constant we have

(3.24)

$$\mu = \sum_{m=1}^{M} \rho_m \sum_{\mathbf{n}\in\mathbb{Z}^3}{}' e^{-t_m||\mathbf{n}||^2}(-1)^{n_1+n_2+n_3} = \sum_{m=1}^{M} \rho_m [\sum_{n\in\mathbb{Z}} (-1)^n\, e^{-t_m n^2}]^3 - \sum_{m=1}^{M} \rho_m.$$

Let us compute the Fourier coefficients for $Q(\tau, x)$, a periodic function with the period 2. We have

$$q_k(\tau) = \frac{1}{2}\int_{-1}^{1} Q(\tau, x)\, e^{-\pi i x k}\, dx,$$

and, extending integration to $(-\infty, +\infty)$,

$$q_k(\tau) = \int_{-\infty}^{\infty} (e^{-4\tau x^2} - e^{-4\tau(x+1/2)^2}) e^{-2\pi i x k} dx = \frac{\sqrt{\pi}}{2\sqrt{\tau}}\, e^{-k^2\pi^2/(4\tau)}(1 - (-1)^k),$$

so that

$$Q(\tau, x) = \sum_{k\in\mathbb{Z}} \frac{\sqrt{\pi}}{\sqrt{\tau}}\, e^{-(k+1/2)^2\pi^2/\tau} e^{2\pi i x(k+1/2)}.$$

Thus, we arrive at (3.23) and an expression for the Madelung constant,

$$\mu = \pi^{3/2} \sum_{m=1}^{M} \rho_m [\sum_{n\in\mathbb{Z}} \frac{1}{\sqrt{t_m}}\, e^{-(n+1/2)^2\pi^2/t_m}]^3 - \sum_{m=1}^{M} \rho_m = -1.7475645946...$$

We note that computing of slowly (conditionally) convergent sum has been reduced to an explicit expression involving only a small number of fast convergent sums over a one-dimentional lattice.

We note that

$$|\frac{1}{||\mathbf{x}||} - \sum_{m=1}^{M} \rho_m\, e^{-t_m||\mathbf{x}||^2}| \le \epsilon$$

outside the ball of radius $1/2$ and, thus, on the boundary of the cube B. Also $Q(t, \pm 1/2) = 0$ for any $t > 0$ so that $G_M^{appr}(\mathbf{x})$ is the Green's function of the homogeneous boundary value problem in B with accuracy ϵ.

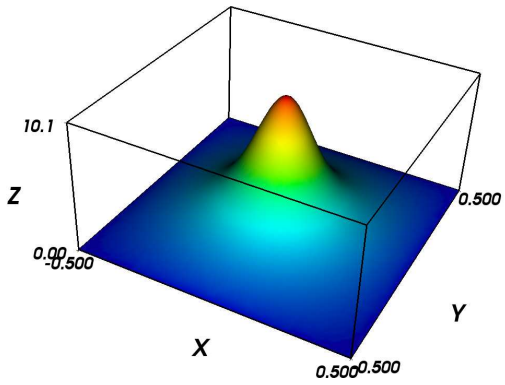


FIGURE 3.2. A periodic part of the external contribution to the Madelung potential (a 2D slice at $z = 0$).

4. Results for Task 2: Representation via Gaussians for two-particle problems

One of the key aspects in our approach is to represent cusps due to electron-electron interaction. For illustration, we consider the simplest two-particle problem, the Helium atom. We have the Hamiltonian,

$$\mathcal{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{||\mathbf{x}_1||} - \frac{2}{||\mathbf{x}_2||} + \frac{1}{||\mathbf{x}_1 - \mathbf{x}_2||}, \tag{4.1}$$

and need to solve the eigenvalue problem,

$$\mathcal{H}\Psi = E\Psi. \tag{4.2}$$

Let us seek the ground state wave function in the form

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \sum \psi_m e^{-\alpha_m ||\mathbf{x}_1||^2 - \beta_m ||\mathbf{x}_1 - \mathbf{x}_2||^2 - \gamma_m ||\mathbf{x}_2||^2}. \tag{4.3}$$

In quantum chemistry such form of the wave function has been used before, see e.g. [37], where the exponents α_m, β_m, γ_m were selected upfront and the coefficients ψ_m computed to minimize the energy.

In our approach we solve for the exponents α_m, β_m, γ_m, the coefficients ψ_m and the number of terms so that the wave function satisfies the equation with a prescribed accuracy. Such approach is feasible since we can show that, after we rewrite (4.2) as an integral equation (similar to what we do in [28, 30, 50, 51]), the form of the wave function (4.3) is preserved under the iteration performed to solve the equation. Since each iteration increases the number of terms, the problem then is to develop an algorithm for reducing the number of terms in the separated representation (4.3).

This leads to the following problem: assuming that we are given a function

$$f(x_1, x_2, \dots x_N) = \sum_{m=1}^{M} w_m e^{-\sum_{j=1}^{N} \tau_{m,j} x_j}, \tag{4.4}$$

where $x_j \in [0,1]$, $\tau_{m,j} > 0$, and $w_m > 0$, find a shorter optimal representation of the same form. Namely, if the number of terms in (4.4) is not optimal for a given accuracy ϵ, find g,

$$g(x_1, x_2, \dots x_N) = \sum_{m=1}^{\hat{M}} \hat{w}_m e^{-\sum_{j=1}^{N} \hat{\tau}_{m,j} x_j}, \tag{4.5}$$

$||f - g|| \leq \epsilon$, such that $\hat{M} < M$.

1. We have solved this problem for $N = 1$ in [14] and have developed a preliminary algorithm for $N = 2$. We now understand analytic and geometric ingredients of this problem. We computed optimal representations in a number of two and three dimensional examples and, currently, we are developing further additional components of the algorithm. For example, for dimensions greater than two, we need to group the initial exponents according to their spatial distribution, and then solve several subproblems. Our results for $N = 2$ should lead to many applications beyond the scope of this project (e.g., generalized Gaussian quadratures for exponentials for 2D domains, thus extending results in [12]).
2. We have developed a new "suboptimal" reduction algorithm and computed several examples for dimension $N = 3$. One of the examples is the numerical construction of an approximation of the Coulomb Green's function. This case is of interest for both Task 1 and Task 2. Such Green's function (which is not a convolution) has an analytic expression known since 1960s providing for us a mechanism to verify our results. We note that the analytic expression itself (e.g. [34],[40]) has not been used in computations.
3. We have now a mathematical framework (with some proofs) for the construction of the multiparticle Green's functions for the so-called Rollnik classes of potentials (see [5]). Such potentials (or their approximations) are sufficient for computations with bound states. This is important on a conceptual and on a practical level (e.g., we obtain convergent algorithms).
4. Our approach is applicable to multi-particle computations (in contrast to using the Gross-Pitaevskii equation) for Bose-Einstein Condensate (BEC).

We now provide a more detailed description of the results.

4.1. **Green's functions for a central potential.** For the Hamiltonian

$$\mathcal{H} = -\frac{1}{2}\nabla^2 - V(r),$$

let us consider the Green's functions

$$G(\mu) = (\mathcal{H} - \mu\mathcal{I})^{-1}$$

and

$$G_0(\mu) = (-\frac{1}{2}\nabla^2 - \mu\mathcal{I})^{-1}.$$

Proposition 4.1. *Let V be a potential of the form*

$$V(||\mathbf{y}||) = \sum_k v_k e^{-u_k||\mathbf{y}||^2},$$

and $\mu < \inf \sigma(\mathcal{H})$, where $\inf \sigma(\mathcal{H})$ is the lower bound of the spectrum of $\mathcal{H}$.

Then for any $\epsilon > 0$ and $\delta > 0$, $\delta < ||\mathbf{x}-\mathbf{y}|| \leq 1$, the Green's function $G(\mu, \mathbf{x}, \mathbf{y})$ has an approximation $\tilde{G}(\mu, \mathbf{x}, \mathbf{y})$,$||G(\mu, \mathbf{x}, \mathbf{y}) - \tilde{G}(\mu, \mathbf{x}, \mathbf{y})|| \leq \epsilon/||\mathbf{x}-\mathbf{y}||$, where

$$\tilde{G}(\mu, \mathbf{x}, \mathbf{y}) = \sum_m w_m \, e^{-a_m||\mathbf{x}||^2 - b_m||\mathbf{x}-\mathbf{y}||^2 - c_m||\mathbf{y}||^2}. \tag{4.6}$$

Remark. If instead of the eigenvalue problem

$$\mathcal{H}\Psi = \lambda\Psi, \tag{4.7}$$

we solve

$$G(\mu)\Psi = \frac{1}{\lambda - \mu}\Psi,$$

then $(E_0 - \mu)^{-1}$ is the largest eigenvalue, where E_0 is the eigenvalue corresponding to the ground state of (4.7). Thus we have $||G(\mu)||_2 = (E_0 - \mu)^{-1} = \text{dist}(\mu, \sigma(\mathcal{H}))$. We can use the power method to find eigenvalues and the overall approach is simply the inverse power method.

The Green's function G satisfies the Lipmann-Schwinger equation,

$$G(\mu) = G_0(\mu) + G_0(\mu)VG(\mu),$$

from which we obtain

$$G = (\mathcal{I} - G_0V)^{-1}G_0 = G_0^{1/2}(\mathcal{I} - G_0^{1/2}VG_0^{1/2})^{-1}G_0^{1/2}.$$

It follows from Proposition 4.4 in Appendix A, that the operator $\mathcal{I} - G_0^{1/2}VG_0^{1/2}$ is positive definite. Also, it readily follows that the operator $G_0^{1/2}VG_0^{1/2}$ is positive definite as well since V is an operator of multiplication by a positive function. This, in turn, implies that $||\mathcal{I} - G_0^{1/2}VG_0^{1/2}|| < 1$.

Following Proposition 4.2 in Appendix A, we have

$$G = G_0^{1/2} \prod_{j=0}^{\infty} (\mathcal{I} + [G_0^{1/2}VG_0^{1/2}]^{2^j}) \, G_0^{1/2}. \tag{4.8}$$

Let us examine the operator $G_0^{1/2}VG_0^{1/2}$. Using Proposition 4.5, we have

$$\begin{aligned}[G_0^{1/2}VG_0^{1/2}](\mathbf{x}, \mathbf{z}) \quad = \quad & \frac{1}{\pi^4}\sum_k v_k \int_{-\infty}^{\infty} ds_1 \int_{-\infty}^{\infty} ds_2 \, e^{-\frac{1}{4}\mu^2(e^{-2s_1}+e^{-2s_2})+2(s_1+s_2)} \\ & \int e^{-||\mathbf{x}-\mathbf{y}||^2 e^{2s_1}} \, e^{-u_k||\mathbf{y}||^2} \, e^{-||\mathbf{y}-\mathbf{z}||^2 e^{2s_2}} d\mathbf{y}.\end{aligned}$$

Using

$$\int_{\mathbb{R}} \exp[-\sum_{j=1}^{N} a_j(x_j - y)^2]dy = \sqrt{\frac{\pi}{\sum_{j=1}^N a_j}} \, \exp[-\frac{1}{\sum_{l=1}^N a_l} \sum_{i>j} a_i a_j (x_i - x_j)^2], \tag{4.9}$$

and 4.1, we obtain

$$\begin{aligned}[G_0^{1/2} V G_0^{1/2}](\mathbf{x},\mathbf{z}) &= \frac{1}{\pi^{5/2}} \sum_k v_k \int_{-\infty}^{\infty} ds_1 \int_{-\infty}^{\infty} ds_2 \, \frac{e^{-\frac{1}{4}\mu^2(e^{-2s_1}+e^{-2s_2})+2(s_1+s_2)}}{(e^{2s_1}+u_k+e^{2s_2})^{3/2}} \\ &\times \quad e^{-\frac{e^{2s_1}u_k}{e^{2s_1}+e^{2s_2}+u_k}||\mathbf{x}||^2 - \frac{e^{2s_1}e^{2s_2}}{e^{2s_1}+e^{2s_2}+u_k}||\mathbf{x}-\mathbf{z}||^2 - \frac{e^{2s_2}u_k}{e^{2s_1}+e^{2s_2}+u_k}||\mathbf{z}||^2}.\end{aligned}$$

This double integral can be discretized using the trapezoidal rule in two dimensions, similar to the construction in [29, 30, 13], to yield an approximate representation of the form stated in (4.14). At this point we are not counting the necessary number of terms, just noting that they are of the desired form. The powers of T_0, $T_0^{2^j}$, as needed in (4.8), will have a similar integral representation with the number of integrals doubling as we step from j to $j+1$. Again, using the trapezoidal rule, we obtain terms of the desired form and, as the number of retained terms in (4.8) is finite for a given accuracy ϵ, the process will terminate after a finite number of terms. Since we use potentials without singularities, the norm $G(\mu,\mathbf{x},\mathbf{y}) - \tilde{G}(\mu,\mathbf{x},\mathbf{y})$ will be controlled by selecting the parameters of the trapezoidal rule. This argument provides the form of the Green's function but not the number of terms.

In order to make this computation practical, we turn to the second part of Proposition 4.2. We have a recursion,

$$\mathcal{Y}_{n+1} = 2\mathcal{Y}_n - \mathcal{Y}_n \left(\mathcal{I} - G_0^{1/2} V G_0^{1/2}\right) \mathcal{Y}_n, \text{ with } \mathcal{Y}_0 = \mathcal{I},$$

where $\mathcal{Y}_n \to (\mathcal{I} - G_0^{1/2} V G_0^{1/2})^{-1}$.

Let us use a representation of the kernel $G_0^{1/2}$ via Gaussians as it follows from Appendix B,

$$G_0^{1/2}(\mu, \mathbf{x}-\mathbf{y}) = \sum_l g_l e^{-s_l||\mathbf{x}-\mathbf{y}||^2}.$$

Computing $G_0^{1/2} V G_0^{1/2}$, we have an approximation

$$\sum_{l,k,l'} g_l v_k g_{l'} \int e^{-s_l||\mathbf{x}-\mathbf{y}||^2} e^{-u_k||\mathbf{y}||^2} \, e^{-s_{l'}||\mathbf{y}-\mathbf{z}||^2} d\mathbf{y} \tag{4.10}$$

Using (4.9), we arrive at

$$\sum_{l,k,l'} g_l v_k g_{l'} \left(\frac{\pi}{s_l + s_{l'} + u_k}\right)^{3/2} e^{-\frac{s_l u_k}{s_l+s_{l'}+u_k}||\mathbf{x}||^2} \, e^{-\frac{s_l s_{l'}}{s_l+s_{l'}+u_k}||\mathbf{x}-\mathbf{z}||^2} \, e^{-\frac{s_{l'}u_k}{s_l+s_{l'}+u_k}||\mathbf{z}||^2}, \tag{4.11}$$

which is of the form in (4.14). We now need to reduce the number of terms in (4.11) and, for this reason, arrive at the following problem: given a function

$$f(x) = \sum_k w_k e^{-a_k^1 x_1 - a_k^2 x_2 - a_k^3 x_3},$$

approximate f by a function $\tilde{f}$ of the same form but with a fewer number of terms.

We note that the form in (4.14) is preserved under further iteration, namely, if we compute the integral (for a single term),

$$I_{lkm} = g_l v_k w_m \int e^{-s_l||\mathbf{x}-\mathbf{y}||^2} e^{-u_k||\mathbf{y}||^2} \, e^{-\tau_m||\mathbf{y}||^2 - \sigma_m||\mathbf{y}-\mathbf{z}||^2 - \xi_m||\mathbf{z}||^2} d\mathbf{y}, \tag{4.12}$$

and use (4.9), we obtain

$$I_{lkm} = g_l v_k w_m (\frac{\pi}{c_{lkm}})^{3/2} \, e^{-\frac{s_l(u_k+\tau_m)}{c_{lkm}}||\mathbf{x}||^2 - \frac{s_l\sigma_m}{c_{lkm}}||\mathbf{x}-\mathbf{z}||^2 - (\xi_m + \frac{(u_k+\tau_m)\sigma_m}{c_{lkm}})||\mathbf{z}||^2}, \tag{4.13}$$

where $c_{lkm} = s_l + u_k + \sigma_m + \tau_m$. This gives us

$$\hat{\tau}_{lkm} = -\frac{s_l(u_k+\tau_m)}{c_{lkm}}, \quad \hat{\sigma}_{lkm} = \frac{s_l\sigma_m}{c_{lkm}}, \quad \hat{\xi}_{lkm} = \xi_m + \frac{(u_k+\tau_m)\sigma_m}{c_{lkm}},$$

and

$$\hat{w}_{lkm} = g_l v_k w_m (\frac{\pi}{c_{lkm}})^{3/2},$$

as new parameters.

4.2. **Green's functions for multiparticle systems.**

4.2.1. *Confining potential.* Consider the Hamiltonian of the system with K nuclei,

$$\mathcal{H} = \sum_{j=1}^{N_e} (-\frac{1}{2}\nabla_j^2 - \sum_{k=1}^{K} \frac{Z_k}{||\mathbf{x}_j - \mathbf{r}_k||}).$$

The Green's function,

$$G(\mu) = (\mathcal{H} - \mu\mathcal{I})^{-1},$$

can be approximated by

$$G(\mu, \mathbf{x}_1, \mathbf{y}_1, \mathbf{x}_2, \mathbf{y}_2, \dots) = \sum_m w_m \prod_j e^{-\sum_k \tau_{m,k}||\mathbf{x}_j - \mathbf{r}_k||^2 - \sigma_m||\mathbf{x}_j - \mathbf{y}_j||^2 - \sum_k \xi_{m,k}||\mathbf{y}_j - \mathbf{r}_k||^2}, \tag{4.14}$$

for $\mu < E_0$, where E_0 is the smallest eigenvalue of $\mathcal{H}$.

4.2.2. *A Hamiltonian with the electron-electron interaction.* Consider the Hamiltonian of the system with K nuclei and N_e electrons,

$$\mathcal{H} = \sum_{j=1}^{N_e} (-\frac{1}{2}\nabla_j^2 - \sum_{k=1}^{K} \frac{Z_k}{||\mathbf{x}_j - \mathbf{r}_k||}) + \sum_{i>j} \frac{1}{||\mathbf{x}_i - \mathbf{x}_j||}.$$

The Green's function,

$$G(\mu) = (\mathcal{H} - \mu\mathcal{I})^{-1},$$

can be approximated by

$$\begin{aligned} G(\mu, \mathbf{x}_1, \mathbf{y}_1, \mathbf{x}_2, \mathbf{y}_2, \dots) &= \sum_m w_m \, e^{-\sum_j [\sum_k a_{m,k}||\mathbf{x}_j - \mathbf{r}_k||^2 + \sum_k b_{m,k}||\mathbf{y}_j - \mathbf{r}_k||^2]} \\ &\times \quad e^{-\sum_{ij} c_{m,ij}||\mathbf{x}_i - \mathbf{y}_j||^2 - \sum_{i>j}[g_{m,ij}||\mathbf{x}_i - \mathbf{x}_j||^2 + f_{m,ij}||\mathbf{y}_i - \mathbf{y}_j||^2]}, \end{aligned} \tag{4.15}$$

for $\mu < E_0$, where E_0 is the smallest eigenvalue of $\mathcal{H}$. We conjecture that it may be possible to simplify,

$$\begin{aligned} G(\mu, \mathbf{x}_1, \mathbf{y}_1, \mathbf{x}_2, \mathbf{y}_2, \dots) &= \sum_m w_m \, e^{-\sum_j \sum_k a_{m,k}(||\mathbf{x}_j - \mathbf{r}_k||^2 + ||\mathbf{y}_j - \mathbf{r}_k||^2)} \\ &\times \quad e^{-\sum_{ij} c_{m,ij}||\mathbf{x}_i - \mathbf{y}_j||^2 - \sum_{i>j} g_{m,ij}(||\mathbf{x}_i - \mathbf{x}_j||^2 + ||\mathbf{y}_i - \mathbf{y}_j||^2)}, \end{aligned} \tag{4.16}$$

4.2.3. *Spectral Projectors.* Representation of a spectral projector computed for the Green's function has the structure as the Green's function itself (unlike the eigenfunctions, which need additional terms or factors to account for momentum indices). We construct the spectral projector from the sign function using

$$P_\mu(\mathbf{x},\mathbf{y}) = \sum_{\lambda_j<\mu} \psi_j(\mathbf{x})\bar{\psi}_j(\mathbf{y}) = (\mathcal{I} - \mathrm{sign}(\mathcal{H} - \mu\mathcal{I}))/2, \tag{4.17}$$

where ψ_j is an orthonormal basis of eigenfunctions and the sign function is defined on $(-\infty,\infty)$ by

$$\mathrm{sign}(\lambda) = \begin{cases} 1 & \lambda > 0 \\ 0 & \lambda = 0 \\ -1 & \lambda < 0 \end{cases}. \tag{4.18}$$

If an operator or its projection on the discrete spectrum are written as

$$\mathcal{H}(\mathbf{x},\mathbf{y}) = \sum_j \lambda_j \psi_j(\mathbf{x})\bar{\psi}_j(\mathbf{y}) \tag{4.19}$$

with λ_j real, then

$$\mathrm{sign}(\mathcal{H})(\mathbf{x},\mathbf{y}) = \sum_j \mathrm{sign}(\lambda_j)\psi_j(\mathbf{x})\bar{\psi}_j(\mathbf{y}). \tag{4.20}$$

4.2.4. *Recursive construction.* We use a polynomial recursion (see e.g. [4, 33, 7]) to compute $\mathrm{sign}(\mathcal{H})$:

$$\begin{aligned} \mathcal{Y}_0 &= \mathcal{H}/||\mathcal{H}||_2 \\ \mathcal{Y}_{k+1} &= (3\mathcal{Y}_k - \mathcal{Y}_k^3)/2, \quad k = 0, 1, \ldots \end{aligned} \tag{4.21}$$

Other polynomials may be used in place of the one above; see [33] for a discussion of the various choices. It is easy to demonstrate that $\mathcal{Y}_k \to \mathrm{sign}(\mathcal{H})$ in (4.21) (see e.g. [7]). The number of iterations needed for (4.21) to converge to accuracy ϵ is $\mathcal{O}(c\log_2\kappa + \log_2\log_2(1/\epsilon))$, where κ is the condition number of $\mathcal{Y}_0$.

We note that computation of the projections via (4.21) has qualitatively different properties than that of the direct computation of individual eigenfunctions. As in the case of the Green's function the iteration in (4.21) does not change the form of the Gaussian representation.

4.2.5. *Bound state solutions of the Lippman-Schwinger Equation.* Consider a self-adjoint operator

$$\mathcal{H} = \mathcal{H}_0 - \mathcal{V} \tag{4.22}$$

and the Green's function

$$\mathcal{G}(z) = (\mathcal{H} - z\mathcal{I})^{-1},$$

for $z \notin \sigma(\mathcal{H})$, where $\sigma(\mathcal{H})$ denotes the spectrum of the operator $\mathcal{H}$. Assuming $z \notin \sigma(\mathcal{H}_0)$ and introducing

$$\mathcal{G}_0(z) = (\mathcal{H}_0 - z\mathcal{I})^{-1},$$

we (formally) have the Lippman-Schwinger equation for $\mathcal{G}$,

$$\mathcal{G} = \mathcal{G}_0 + \mathcal{G}_0\mathcal{V}\mathcal{G},$$

or $\mathcal{G} = (\mathcal{I} - \mathcal{G}_0\mathcal{V})^{-1}\mathcal{G}_0$. Alternatively, we can write

$$\mathcal{G} = \mathcal{G}_0^{1/2}(\mathcal{I} - \mathcal{G}_0^{1/2}\mathcal{V}\mathcal{G}_0^{1/2})^{-1}\mathcal{G}_0^{1/2}.$$

To construct $(\mathcal{I} - \mathcal{G}_0^{1/2}\mathcal{V}\mathcal{G}_0^{1/2})^{-1}$, we will use

Proposition 4.2. 1. *If $\mathcal{B}$ is a bounded positive definite operator, then its inverse has a product representation*

$$\mathcal{B}^{-1} = \kappa \prod_{j=0}^{\infty} [\mathcal{I} + (\mathcal{I} - \kappa\mathcal{B})^{2^j}], \tag{4.23}$$

where $\kappa < 1/||\mathcal{B}||$.

2. *The iteration*

$$\mathcal{Y}_{n+1} = 2\mathcal{Y}_n - \mathcal{Y}_n\,\mathcal{B}\,\mathcal{Y}_n, \;\; \textit{with} \;\; \mathcal{Y}_0 = \kappa\mathcal{I},$$

converges quadratically to the inverse, $\mathcal{Y}_n \to \mathcal{B}^{-1}$ as $n \to \infty$ and

$$\mathcal{Y}_{n+1} = \kappa \prod_{j=0}^{n} [\mathcal{I} + (\mathcal{I} - \kappa\mathcal{B})^{2^j}], \quad n = 0, 1, \ldots.$$

Proof. We have $\mathcal{B}^{-1} = \kappa(\mathcal{I} - (\mathcal{I} - \kappa\mathcal{B}))^{-1}$. Since $\mathcal{B}$ is a bounded positive definite operator, selecting $\kappa < 1/||\mathcal{B}||$ implies that $||\mathcal{I} - \kappa\mathcal{B}|| < 1$. Using the product form of the converging series $\mathcal{B}^{-1} = \kappa[\mathcal{I} + (\mathcal{I} - \kappa\mathcal{B}) + (\mathcal{I} - \kappa\mathcal{B})^2 + \ldots]$, we obtain (4.23). The iteration simply generates the same product as in (4.23). □

Proposition 4.3.

1. Let $\mathcal{B}$ be a bounded operator. If the inverse operator $\mathcal{B}^{-1}$ exists, then it has a product representation

$$\mathcal{B}^{-1} = \kappa \prod_{j=0}^{\infty} [\mathcal{I} + (\mathcal{I} - \kappa\mathcal{B}^*\mathcal{B})^{2^j}]\mathcal{B}^*, \tag{4.24}$$

where $\kappa < 1/||\mathcal{B}^*\,\mathcal{B}||$.

(a) The iteration

$$\mathcal{Y}_{n+1} = 2\mathcal{Y}_n - \mathcal{Y}_n\,\mathcal{B}\,\mathcal{Y}_n, \;\; \text{with} \;\; \mathcal{Y}_0 = \kappa\mathcal{B}^*,$$

converges quadratically to the inverse, $\mathcal{Y}_n \to \mathcal{B}^{-1}$ as $n \to \infty$ and

$$\mathcal{Y}_{n+1} = \kappa \prod_{j=0}^{n} [\mathcal{I} + (\mathcal{I} - \kappa\mathcal{B}^*\mathcal{B})^{2^j}]\mathcal{B}^*, \quad n = 0, 1, \ldots.$$

Proof. We have $\mathcal{B}^{-1} = (\mathcal{B}^*\mathcal{B})^{-1}\mathcal{B}^*$. Since $\mathcal{B}^*\mathcal{B}$ is a bounded positive definite operator, we use Proposition 4.2 to compute $(\mathcal{B}^*\mathcal{B})^{-1}$. □

Proposition 4.4. *If the potential $\mathcal{V}$ is in the Rollnik class and $z \notin \sigma(\mathcal{H})$, then $\mathcal{B} = \mathcal{I} - \mathcal{G}_0^{1/2}(z)\mathcal{V}\mathcal{G}_0^{1/2}(z)$ is a bounded operator. If $z \in \mathbb{R}$ and $z < \min(\sigma(\mathcal{H}))$, then $\mathcal{B}$ is a positive definite operator and $\|\mathcal{G}_0^{1/2}(z)\mathcal{V}\mathcal{G}_0^{1/2}(z)\| < 1$.*

Proof. Let us consider the inner product $(\mathcal{B}x, x) = (x, x) + (\mathcal{V}\mathcal{G}_0^{1/2}x, \mathcal{G}_0^{1/2}x)$. Setting $y = \mathcal{G}_0^{1/2}x$, we have

$$(\mathcal{B}x, x) = (\mathcal{G}_0^{-1/2}y, \mathcal{G}_0^{-1/2}y) + (\mathcal{V}y, y) = (\mathcal{G}_0^{-1}y, y) + (\mathcal{V}y, y) = ((\mathcal{H} - z\mathcal{I})y, y) > 0$$

for any x. Since $\mathcal{G}_0^{1/2}(z)\mathcal{V}\mathcal{G}_0^{1/2}(z)$ is also positive definite implies that $\|\mathcal{G}_0^{1/2}(z)\mathcal{V}\mathcal{G}_0^{1/2}(z)\| < 1$. □

Using Proposition we have that if $\mathcal{B}$ is bounded, then

$$\mathcal{G} = \kappa \mathcal{G}_0^{1/2} \prod_{j=0}^{\infty} (\mathcal{I} + [(1-\kappa)\mathcal{I} + \kappa \mathcal{G}_0^{1/2} \mathcal{V} \mathcal{G}_0^{1/2}]^{2^j}) \, \mathcal{G}_0^{1/2}. \tag{4.25}$$

If $\|\mathcal{G}_0^{1/2}(z)\mathcal{V}\mathcal{G}_0^{1/2}(z)\| < 1$ then $\|\mathcal{B}\| < 1$ and we choose $\kappa = 1$ to obtain from (4.25)

$$\mathcal{G} = \mathcal{G}_0^{1/2} \prod_{j=0}^{\infty} (\mathcal{I} + [\mathcal{G}_0^{1/2} \mathcal{V} \mathcal{G}_0^{1/2}]^{2^j}) \, \mathcal{G}_0^{1/2}, \tag{4.26}$$

an alternative of the usual Born series.

4.2.6. *Integral Representation and Approximation of* $\mathcal{G}_0^{\alpha}$. In problems of quantum mechanics we choose

$$\mathcal{H}_0 = -\frac{1}{2}\nabla^2,$$

and construct an approximation of the kernel of $\mathcal{G}_0^{\alpha}$, $\alpha > 0$, where

$$\mathcal{G}_0(\lambda) = (\mathcal{H}_0 - \lambda \mathcal{I})^{-1}.$$

We first recall the kernel of $e^{t\nabla^2}$, the heat kernel,

$$K_{e^{t\nabla^2}}(\mathbf{x}-\mathbf{y}) = (4\pi t)^{-\frac{3}{2}} e^{-\frac{1}{4}\|\mathbf{x}-\mathbf{y}\|^2 t^{-1}}, \tag{4.27}$$

and the integral representation of the positive powers of a self-adjoint positive definite operator,

$$L^{-\alpha} = \frac{1}{\Gamma(\alpha)} \int_0^{\infty} e^{-tL} t^{\alpha-1} dt.$$

We have for $\lambda = -\frac{1}{2}\mu^2 < 0$,

$$\mathcal{G}_0^{\alpha} = (-\frac{1}{2}\nabla^2 + \frac{1}{2}\mu^2 \mathcal{I})^{-\alpha} = \frac{2^{\alpha}}{\Gamma(\alpha)} \int_0^{\infty} e^{t\nabla^2} e^{-\mu^2 t} t^{\alpha-1} dt.$$

Using (4.27), we have

$$\mathcal{G}_0^{\alpha}(\mathbf{x}-\mathbf{y}) = \frac{2^{\alpha}}{\Gamma(\alpha)(4\pi)^{\frac{3}{2}}} \int_0^{\infty} e^{-\mu^2 t} e^{-\frac{1}{4t}\|\mathbf{x}-\mathbf{y}\|^2} t^{\alpha-\frac{5}{2}} dt. \tag{4.28}$$

Since

$$\int_0^{\infty} e^{-a^2 t} e^{-\frac{1}{4t}b^2} t^{c-1} dt = 2^{1-c} (\frac{b}{a})^c \mathrm{K}_c(ab) = 2^{1-c} (\frac{b}{a})^c \mathrm{K}_{-c}(ab), \tag{4.29}$$

where K_{α} is the modified Bessel function of the second kind. This formula follows from [27, Formula 8.432(6)] ,

$$\mathrm{K}_c(z) = 2^{c-1} z^{-c} \int_0^{\infty} e^{-t} e^{-\frac{1}{4t}z^2} t^{c-1} dt, \text{ for } |\arg z| < \frac{\pi}{2}, \, \Re z^2 > 0.$$

Thus, $\mathcal{G}_0^{\alpha}$ is a radial function that can be explicitely described as

$$\mathcal{G}_0^{\alpha}(x) = \frac{2^{-\frac{1}{2}}}{\Gamma(\alpha)\pi^{\frac{3}{2}}} (\frac{\mu}{r})^{\frac{3}{2}-\alpha} \mathrm{K}_{\frac{3}{2}-\alpha}(\mu r),$$

where $r = |\mathbf{x}|$. In particular,

$$\mathcal{G}_0(\mathbf{x}) = \frac{1}{2\pi} \frac{e^{-\mu|\mathbf{x}|}}{|\mathbf{x}|}$$

and

$$\mathcal{G}_0^2(\mathbf{x}) = \frac{1}{2\pi\mu} e^{-\mu|\mathbf{x}|}.$$

To approximate $\mathcal{G}_0^\alpha$ as a sum of Gaussians, we change variables $t = e^{-2s}/4$ in (4.28) to obtain

Proposition 4.5. *The kernel of $\mathcal{G}_0^\alpha$ has an integral representation*

$$\mathcal{G}_0^\alpha(\mathbf{x}-\mathbf{y}) = \frac{2^{1-\alpha}}{\Gamma(\alpha)\pi^{\frac{3}{2}}} \int_{-\infty}^{\infty} e^{-\|\mathbf{x}-\mathbf{y}\|^2 e^{2s}} e^{-\frac{1}{4}\mu^2 e^{-2s} + (3-2\alpha)s} ds. \tag{4.30}$$

For $\alpha = 1$ we obtain from (4.30) a familiar representation (see [29, 30, 13]*),*

$$\mathcal{G}_0(\mathbf{x}-\mathbf{y}) = \frac{1}{\pi^{\frac{3}{2}}} \int_{-\infty}^{\infty} e^{-\|\mathbf{x}-\mathbf{y}\|^2 e^{2s}} e^{-\frac{1}{4}\mu^2 e^{-2s} + s} ds,$$

and, for $\alpha = 1/2$, an integral representation for the kernel of $\mathcal{G}_0^{1/2}$,

$$\mathcal{G}_0^{1/2}(\mathbf{x}-\mathbf{y}) = \frac{2^{\frac{1}{2}}}{\pi^2} \int_{-\infty}^{\infty} e^{-\|\mathbf{x}-\mathbf{y}\|^2 e^{2s}} e^{-\frac{1}{4}\mu^2 e^{-2s} + 2s} ds.$$

5. Results for Task 3: Multiparticle Schrödinger Equation

This part of the project is the beginning of the program to develop accurate methods for solving equations of multiparticle quantum mechanics. In this section we will descibe what was accomplished, compare with existing state of the art, and indicate directions of further development.

Our goal was specifically to address the issue of size-consistency. We first developed a "center-of-mass" principle upon which an algorithmic size-consistent method can be built. We were then advised that the inter-electron cusp was a crucial issue, and so we developed a principle upon which a method capturing this cusp can be built. As these methods were becoming large and complex, we went back and worked on the details of the basic method upon which they were grown, namely the use of separated representations for wavefunctions. In the next section we give a technical introduction to the multiparticle Schrödinger, and the outline of how separated representations can be used to approximate the wavefunction. The following section sketches the method for size-consistency, and the final section comments on the inter-electron cusp.

5.1. Technical introduction; Approximating the Wavefunction with an unconstrained sum of Slater Determinants.

The multiparticle Schrödinger equation is the basic governing equation in quantum mechanics. We consider the time-independent case, and fix the nuclei according to the Born-Oppenheimer approximation, so the equation describes the steady state of an interacting system of electrons. For each of the N electrons in the system there are three spatial variables $\mathbf{r} = (x, y, z)$, and a discrete spin variable σ taking the values $\{-\frac{1}{2}, \frac{1}{2}\}$, which we combine and denote $(\mathbf{r}, \sigma)$ by γ. The Hamiltonian operator $\mathcal{H}$ is a sum of a kinetic energy operator $\mathcal{T}$, a nuclear potential operator $\mathcal{V}$, and an electron-electron interaction operator $\mathcal{W}$, defined by

$$\mathcal{H} = \mathcal{T} + \mathcal{V} + \mathcal{W} = -\frac{1}{2}\sum_{i=1}^{N} \Delta_i + \sum_{i=1}^{N} v(\mathbf{r}_i) + \frac{-1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N} \frac{1}{\|\mathbf{r}_i - \mathbf{r}_j\|}, \tag{5.1}$$

where Δ_i is the three-dimensional Laplacian acting in the variable $\mathbf{r}_i$ and $v(\mathbf{r})$ is a sum of terms of the form $z_a/\|\mathbf{r}-\mathbf{R}_a\|$ from a nucleus at position $\mathbf{R}_a$ with charge z_a. The antisymmetric eigenfunctions of $\mathcal{H}$ represent electronic states of the system and are called wavefunctions. Antisymmetric means that under the exchange of any two coordinates, the wavefunction is odd, e.g. $\psi(\gamma_2,\gamma_1,\dots)=-\psi(\gamma_1,\gamma_2,\dots)$. The bound-state wavefunctions have negative eigenvalues, and are of greatest interest, so we will focus on the wavefunction with the most negative eigenvalue. In summary, our goal is to find the most negative (discrete) eigenvalue

$$\mathcal{H}\psi=\lambda\psi\,, \tag{5.2}$$

subject to the antisymmetry condition on ψ.

Analytic methods can give qualitative results about its solutions, and determine limiting cases, but most quantitative results must be obtained numerically. Although the equation is a 'simple' eigenvalue problem, its numerical solution presents several serious difficulties, among them the large number of variables and the antisymmetry condition on the solution. The simplest method that addresses these two difficulties is Hartree-Fock (HF), which uses the antisymmetrization of a single product to approximate the N-particle wavefunction, i.e.,

$$\psi_{\mathrm{HF}}=\mathcal{A}\prod_{i=1}^{N}\phi_i(\gamma_i)\,. \tag{5.3}$$

Any approximation $\tilde{\psi}$ to the wavefunction ψ can be substituted into

$$\frac{\langle\mathcal{H}\tilde{\psi},\tilde{\psi}\rangle}{\|\tilde{\psi}\|} \tag{5.4}$$

to obtain an upper bound on the lowest value of λ that solves (5.2). Substituting (5.3) into (5.4), one can derive a system of equations for ϕ_i to minimize (5.4). The resulting ψ_{HF} will best approximate ψ, in the sense of providing the best estimate (5.4).

To improve upon HF, it is natural to consider a sum of products

$$\psi_{(r)}=\mathcal{A}\sum_{l=1}^{r}s_l\prod_{i=1}^{N}\phi_i^l(\gamma_i)\,. \tag{5.5}$$

The coefficients s_l are not strictly necessary, but they allow us to assume $\|\phi_i^l\|=1$. Many methods are based on this form, and the distinction is in how they use it. The Configuration Interaction (CI) method (see e.g. [48]) chooses the functions ϕ_i^l from a preselected master set of orthogonal functions and decides on a large number r of combinations to consider, based on excitation level. Substituting (5.5) into (5.4) leads to a matrix eigenvalue problem that can be solved for the scalar coefficients s_l. The Multi-Configuration Self-Consistent Field (MCSCF) method (e.g. [24, 17]), chooses a pattern of excitations similar to CI, but then solves for the master set of orthogonal functions as well as the scalar coefficients. Many variations and combinations of these methods have been developed, and indeed there is a whole industry in producing them.

We demonstrate a method that also uses a wavefunction of the form (5.5) but without constraints such as orthogonality on the ϕ_i^l. By removing these constraints we produce much better approximations at much smaller r than existing methods allow. In another context [11] we have given examples where removing constraints

produces expansions that are *exponentially* more efficient, i.e. $r = N$ instead of 2^N or $r = \log N$ instead of N. For example, in our approach we can have a two-term representation

$$\begin{aligned} & \phi_1(\gamma_1)\phi_2(\gamma_2)\cdots\phi_N(\gamma_N) \\ +c \quad & [\phi_1(\gamma_1)+\phi_{N+1}(\gamma_1)][\phi_2(\gamma_2)+\phi_{N+2}(\gamma_2)]\cdots[\phi_N(\gamma_N)+\phi_{2N}(\gamma_N)]\,, \end{aligned} \tag{5.6}$$

where $\{\phi_j\}_{j=1}^{2N}$ form an orthonormal set. To represent (5.6) while requiring all factors to come from a master orthogonal set would force one to multiply out the second term and thus obtain a representation with 2^N terms. It is common sense that removal of constraints could produce better results, and steps in that direction have been taken (e.g.[46, 1, 23, 19, 20, 52, 42]). These works, however, were only able to partially remove the constraints, and so, we claim, did not achieve the full potential.

We will use a Green's function iteration to move a trial wavefunction toward the minimum of (5.4) without using (5.4) directly. This iteration was introduced in [36, 35] and used in e.g.[30]. Define the Green's function

$$\mathcal{G}_\mu = (\mathcal{T} - \mu\mathcal{I})^{-1}\,, \tag{5.7}$$

for $\mu < 0$. The Green's function iteration is

$$\begin{aligned} g_n &= -\mathcal{G}_{\mu_n}[(\mathcal{V}+\mathcal{W})f_n] \\ \mu_{n+1} &= \mu_n - \langle(\mathcal{V}+\mathcal{W})f_n, f_n - g_n\rangle/\|g_n\|^2 \\ f_{n+1} &= g_n/\|g_n\|. \end{aligned} \tag{5.8}$$

The Green's function iteration is essentially an inverse power method. The convergence rate is only linear, but if the initial μ can be chosen near to but less than the lowest eigenvalue, then the error will decrease by a substantial fraction at each iteration, and not many iterations will be needed. We use I to denote the number of Green's function iterations needed.

We use approximate wavefunctions of the form (5.5), with r fixed. The iteration (5.8) does not directly produce an approximation of the same form, so we modify it by defining g_n to be the function of the form (5.5) that minimizes

$$\|g_n - (-\mathcal{G}_{\mu_n}[(\mathcal{V}+\mathcal{W})f_n])\|. \tag{5.9}$$

In order to assure convergence to an antisymmetric solution, we use the pseudo-norm induced by the pseudo inner product $\langle\cdot,\cdot\rangle_{\mathcal{A}} = \langle\mathcal{A}(\cdot),\mathcal{A}(\cdot)\rangle$, as we did in [11]. Constructing g_n is the most challenging part of the method, and requires the bulk of our effort. To simplfy notation, we now suppress the iteration index n and set $\psi = f_n$ and $\tilde{\psi} = g_n$.

We begin with some approximation $\tilde{\psi}$ (such as ψ itself) and will iteratively improve it. The outermost loop of our iteration is simply to repeat our refinement until it appears that $\tilde{\psi}$ has converged. For the computational cost estimates we denote the number of repetitions by K. To refine our representation we loop through the variables (electrons). The functions in variables other than the current variable are fixed, and the functions in the current variable will be modified to minimize the overall error $\|\tilde{\psi} - \psi\|_{\mathcal{A}}$. This Alternating Least-Squares (ALS) approach is well-known (see e.g. [31, 39, 41, 16, 18, 49]). We will alternate through the directions, but for ease of exposition we describe the $k = 1$ case. So, $\tilde{\phi}_k^l$ is fixed for $k > 1$, and we will solve for the values of $\tilde{\phi}_1^l$ for all l.

To refine in the current variable, we set up and solve a linear least-squares problem. The normal equations for a least-squares problem are derived by taking a gradient with respect to the free parameters and setting this equal to zero. As long as $\tilde{\psi}$ is linear and not degenerate in these parameters, the resulting equations are linear and have a unique solution. Usually these free parameters are coefficients of the representation in some basis. We instead take the parameters to be the point values of our functions ϕ_1^l, or, formally, as the coefficients of the point evaluation functional $\langle\gamma\rangle$. The formulas that we derive can be used with a fixed basis, but are stated independent of the basis. We still obtain linear normal equations

$$\mathbb{A}\mathbf{x} = \mathbf{b}\,, \tag{5.10}$$

but now $b(l)$ is a function of γ, $x(l')$ is a function of γ', and $A(l,l')$ is an integral operator mapping functions of γ' to functions of γ. The kernel of $\mathbb{A}$ is defined by

$$A(l,l')(\gamma,\gamma') = \left\langle \langle\gamma'\rangle \prod_{i=2}^{N} \tilde{\phi}_i^{l'}, \langle\gamma\rangle \prod_{i=2}^{N} \tilde{\phi}_i^{l} \right\rangle_{\mathcal{A}}\,, \tag{5.11}$$

where the point evaluation functionals are acting in the $i = 1$ direction. The functions in $\mathbf{b}$ are defined by

$$b(l)(\gamma) = \sum_{m}^{r} s_m \left\langle -\mathcal{G}_\mu[\mathcal{V}+\mathcal{W}] \prod_{i=1}^{N} \phi_i^m, \langle\gamma\rangle \prod_{i=2}^{N} \tilde{\phi}_i^{l} \right\rangle_{\mathcal{A}}\,. \tag{5.12}$$

Once $\mathbb{A}$ and $\mathbf{b}$ have been constructed, we will apply the Conjugate Gradient iterative method (see e.g. [26]) to solve (5.10). We initialize with $\mathbf{r} = \mathbf{b} - \mathbb{A}\mathbf{x}$, $\mathbf{v} = \mathbf{r}$, and $c = \langle\mathbf{r},\mathbf{r}\rangle$, and then the core of the method is the sequence of assignments $\mathbf{z} \leftarrow \mathbb{A}\mathbf{v}$, $t \leftarrow c/\langle\mathbf{v},\mathbf{z}\rangle$, $\mathbf{x} \leftarrow \mathbf{x}+t\mathbf{v}$, $\mathbf{r} \leftarrow \mathbf{r}-t\mathbf{z}$, $d \leftarrow \langle\mathbf{r},\mathbf{r}\rangle$, $\mathbf{v} \leftarrow \mathbf{r}+(d/c)\mathbf{v}$, and $c \leftarrow d$, applied iteratively. We use S to denote the number of conjugate gradiant iterations needed. Thus $\mathbf{x}$ is constructed using only matrix-vector products and vector additions, all which are compatible with our formulation with integral operators. The conjugate gradient method applies only to positive-definite operators. Our operator $\mathbb{A}$ is only semidefinite due to the nullspace in the antisymmetric pseudonorm. Fortunately, $\mathbf{b}$ was computed with the same pseudonorm and has no component in the nullspace of $\mathbb{A}$.

One advantage of using this iterative method with integral operators is that our algorithm is "basis-free". The representation of $\mathbf{x}$ can naturally be adaptive in γ, for example refining near the nuclei as indicated by the refinement in $\mathbf{b}$. For the estimates of computational cost, we use M to denote the cost to represent a function of γ, or integrate such a function. The antisymmetry contraint requires $N \leq M$, and in general we expect M to be much larger than N. For our numerical results, we use adaptive polynomial multiwavelets, following [28, 30]. In those works it was shown that this basis effectively eliminates basis-set error within HF.

We are left with the problem of how to construct $\mathbb{A}$ in (5.11) and $\mathbf{b}$ in (5.12). We haved develop the machinery and algorithms for computing these antisymmetric inner products. Our formulation uses low-rank perturbations of matrices, thus avoiding cofactor expansions.

The computational cost for the whole method is acceptable. As noted above, the cost depends on N, r, M, I, K, and S. Although S in theory could be as many as rM, we have a very good starting point, and so expect only a very small constant number to be needed. We use $M \log M$ to denote the cost to convolve a function

of γ with $1/\|\mathbf{r}\|$. Some Poisson solvers achieve this complexity, but this cost may vary with the choice of basis. We use L to denote the number of terms used to approximate the Green's function with Gaussians. The final computational cost is then

$$\mathcal{O}(KIr^2N^2[L(N + M\log M) + S(N + M)]). \tag{5.13}$$

For comparison, the cost to evaluate a single instance of Löwdin's rules is $\mathcal{O}(N^2(N+M))$. The size r needed in practice, and how it depends on the various parameters in the problem, is still an open question.

We are working on initial implementation to verify the correctness of the formulas and algorithms that we have developed.

5.2. **Algorithmic Size-Consistency.** Consider the situation where our system consists of K non-interacting (i.e. well-separated) subsystems, each with N electrons. Suppose that each subsystem has a separated representation ψ_i. The wavefunction for the entire system is

$$\psi \approx \prod_{j=1}^{K} \psi_i.$$

Its inherent complexity grows linearly with K. If each ψ_i has separation rank r, then in order to represent the overall wavefunction in the separated representation we have to multiply out, and so obtain r^K terms. Thus, this representation is not size-consistent. (The terms "size-extensivity" and "size-consistency" are often confused in the literature, but it appears that we actually address "size-consistency".) For a fixed accuracy, we want the computational complexity to scale (nearly) linearly with system size. In classical particle systems, such scaling can be achieved via organizing particles into hierarchical groups and computing the interaction between these groups via e.g., multipole expansions. In the simplest case, this amounts to replacing

Active

Distant

with

Active

Summary

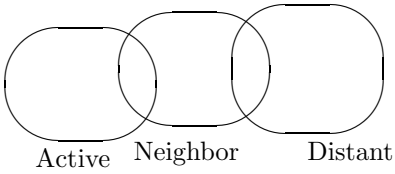
The notion of groups is fairly straightforward in quantum mechanics, and in the non-interacting case we can simply not multiply out the component wavefunctions, and thus obtain a size-consistent representation. Non-interacting systems are not very interesting of course, but they give us the inspiration to use the form

$$\psi \approx \sum_{l=1}^{r} \prod_{j=1}^{K} \psi_i^l$$

for interacting systems. One could plug this back into itself and do more levels.

In quantum-mechanical systems, the interaction between particles is much more complicated, mainly due to the antisymmetry constraint which allows "exchange" of particles. The interactions are thus nonlocal and nonlinear, so a straightforward

generalization of the approach to classical particle systems is not available. In particular, if we have a geometry like



then we cannot compute the effect of the distant group on the active group without accounting for exchange via the neighbor group. Within our ALS method, the key ingredient for achieving size-consistency is to have the marginal cost of each antisymmetric inner product be independent of the total number of groups, so that the total cost scales (nearly) linearly in K. This goal can be accomplished if the effect of distant groups can be summarized and then re-used.

We now demonstrate how to summarize in the case of three groups, by computing

$$\left\langle (\sum_{l_1} \Phi_1^{l_1})(\sum_{l_2} \Phi_2^{l_2})(\sum_{l_3} \Phi_3^{l_3}),(\sum_{l_1'} \tilde{\Phi}_1^{l_1'})(\sum_{l_2'} \tilde{\Phi}_2^{l_2'})(\sum_{l_3'} \tilde{\Phi}_3^{l_3'}) \right\rangle_{\mathcal{A}} .$$

We use $\Phi_1^{l_1}$ to denote the l_1 term in group 1, and so on. We define $\mathbb{L}(\tilde{\Phi}_1^{l_1'}, \Phi_1^{l_1})$ to be the matrix of inner products of the single electron functions, as used in Löwdin's rules. Using Löwdin's rules and our assumption on supports, we have

$$\sum_{l_1,l_1'} \sum_{l_2,l_2'} \sum_{l_3,l_3'} \begin{vmatrix} \mathbb{L}(\tilde{\Phi}_1^{l_1'}, \Phi_1^{l_1}) & \mathbb{L}(\tilde{\Phi}_1^{l_1'}, \Phi_2^{l_2}) & 0 \\ \mathbb{L}(\tilde{\Phi}_2^{l_2'}, \Phi_1^{l_1}) & \mathbb{L}(\tilde{\Phi}_2^{l_2'}, \Phi_2^{l_2}) & \mathbb{L}(\tilde{\Phi}_2^{l_2'}, \Phi_3^{l_3}) \\ 0 & \mathbb{L}(\tilde{\Phi}_3^{l_3'}, \Phi_2^{l_2}) & \mathbb{L}(\tilde{\Phi}_3^{l_3'}, \Phi_3^{l_3}) \end{vmatrix} .$$

The off-diagonal blocks should have rank approximately the number of chemical bonds between the groups. To demonstrate the principle, we will suppose that the rank is one. Applying the inverse of the diagonal blocks, we obtain

$$\sum_{l_1,l_1'} \sum_{l_2,l_2'} \sum_{l_3,l_3'} |\mathbb{L}(\tilde{\Phi}_1^{l_1'}, \Phi_1^{l_1})||\mathbb{L}(\tilde{\Phi}_2^{l_2'}, \Phi_2^{l_2})||\mathbb{L}(\tilde{\Phi}_3^{l_3'}, \Phi_3^{l_3})|$$
$$\begin{vmatrix} \mathbb{I} & \mathbf{u}_{12}^{l_1 l_1' l_2} (\mathbf{v}_{12}^{l_1 l_1' l_2})^* & 0 \\ \mathbf{u}_{21}^{l_1 l_2 l_2'} (\mathbf{v}_{21}^{l_1 l_2 l_2'})^* & \mathbb{I} & \mathbf{u}_{23}^{l_2 l_2' l_3} (\mathbf{v}_{23}^{l_2 l_2' l_3})^* \\ 0 & \mathbf{u}_{32}^{l_2 l_3 l_3'} (\mathbf{v}_{32}^{l_2 l_3 l_3'})^* & \mathbb{I} \end{vmatrix} .$$

We now transform the determinant using the following lemma.

Lemma 5.1. *(Determinant of a Low-Rank Perturbation of the Identity) Let* $\{\mathbf{u}_q\}_{q=1}^Q$ *and* $\{\mathbf{v}_q\}_{q=1}^Q$ *be two sets of vectors. Then*

$$\left| \mathbb{I} + \sum_{q=1}^{Q} \mathbf{u}_q \mathbf{v}_q^* \right| = \begin{vmatrix} 1 + \mathbf{v}_1^* \mathbf{u}_1 & \mathbf{v}_1^* \mathbf{u}_2 & \cdots & \mathbf{v}_1^* \mathbf{u}_Q \\ \mathbf{v}_2^* \mathbf{u}_1 & 1 + \mathbf{v}_2^* \mathbf{u}_2 & \cdots & \mathbf{v}_2^* \mathbf{u}_Q \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{v}_Q^* \mathbf{u}_1 & \mathbf{v}_Q^* \mathbf{u}_2 & \cdots & 1 + \mathbf{v}_Q^* \mathbf{u}_Q \end{vmatrix} .$$

Applying this lemma the final determinant becomes

$$\begin{vmatrix} 1 & (\mathbf{v}_{21}^{l_1 l_2 l_2'})^* \mathbf{u}_{12}^{l_1 l_1' l_2} & 0 & 0 \\ (\mathbf{v}_{12}^{l_1 l_1' l_2})^* \mathbf{u}_{21}^{l_1 l_2 l_2'} & 1 & 0 & (\mathbf{v}_{32}^{l_2 l_3 l_3'})^* \mathbf{u}_{21}^{l_1 l_2 l_2'} \\ (\mathbf{v}_{12}^{l_1 l_1' l_2})^* \mathbf{u}_{23}^{l_2 l_2' l_3} & 0 & 1 & (\mathbf{v}_{32}^{l_2 l_3 l_3'})^* \mathbf{u}_{23}^{l_2 l_2' l_3} \\ 0 & 0 & (\mathbf{v}_{23}^{l_2 l_2' l_3})^* \mathbf{u}_{32}^{l_2 l_3 l_3'} & 1 \end{vmatrix},$$

which can be expanded as

$$\begin{vmatrix} 1 & (\mathbf{v}_{21}^{l_1 l_2 l_2'})^* \mathbf{u}_{12}^{l_1 l_1' l_2} \\ (\mathbf{v}_{12}^{l_1 l_1' l_2})^* \mathbf{u}_{21}^{l_1 l_2 l_2'} & 1 \end{vmatrix} \begin{vmatrix} 1 & (\mathbf{v}_{32}^{l_2 l_3 l_3'})^* \mathbf{u}_{23}^{l_2 l_2' l_3} \\ (\mathbf{v}_{23}^{l_2 l_2' l_3})^* \mathbf{u}_{32}^{l_2 l_3 l_3'} & 1 \end{vmatrix}$$

$$- ((\mathbf{v}_{12}^{l_1 l_1' l_2})^* \mathbf{u}_{23}^{l_2 l_2' l_3})((\mathbf{v}_{21}^{l_1 l_2 l_2'})^* \mathbf{u}_{12}^{l_1 l_1' l_2})((\mathbf{v}_{23}^{l_2 l_2' l_3})^* \mathbf{u}_{32}^{l_2 l_3 l_3'})((\mathbf{v}_{32}^{l_2 l_3 l_3'})^* \mathbf{u}_{21}^{l_1 l_2 l_2'}).$$

Inserting this expansion and rearranging, the first term yields

$$\sum_{l_1, l_1'} |\mathbb{L}(\tilde{\Phi}_1^{l_1'}, \Phi_1^{l_1})| \sum_{l_2, l_2'} |\mathbb{L}(\tilde{\Phi}_2^{l_2'}, \Phi_2^{l_2})| \begin{vmatrix} 1 & (\mathbf{v}_{21}^{l_1 l_2 l_2'})^* \mathbf{u}_{12}^{l_1 l_1' l_2} \\ (\mathbf{v}_{12}^{l_1 l_1' l_2})^* \mathbf{u}_{21}^{l_1 l_2 l_2'} & 1 \end{vmatrix}$$

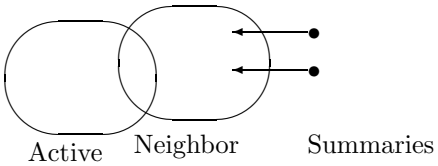
$$\left(\sum_{l_3, l_3'} |\mathbb{L}(\tilde{\Phi}_3^{l_3'}, \Phi_3^{l_3})| \begin{vmatrix} 1 & (\mathbf{v}_{32}^{l_2 l_3 l_3'})^* \mathbf{u}_{23}^{l_2 l_2' l_3} \\ (\mathbf{v}_{23}^{l_2 l_2' l_3})^* \mathbf{u}_{32}^{l_2 l_3 l_3'} & 1 \end{vmatrix} \right),$$

and the second term yields

$$- \sum_{l_1, l_1' l_2, l_2'} \sum ((\mathbf{v}_{21}^{l_1 l_2 l_2'})^* \mathbf{u}_{12}^{l_1 l_1' l_2}) |\mathbb{L}(\tilde{\Phi}_1^{l_1'}, \Phi_1^{l_1})| |\mathbb{L}(\tilde{\Phi}_2^{l_2'}, \Phi_2^{l_2})|$$

$$(\mathbf{v}_{12}^{l_1 l_1' l_2})^* \left(\sum_{l_3, l_3'} \mathbf{u}_{23}^{l_2 l_2' l_3} ((\mathbf{v}_{23}^{l_2 l_2' l_3})^* \mathbf{u}_{32}^{l_2 l_3 l_3'}) |\mathbb{L}(\tilde{\Phi}_3^{l_3'}, \Phi_3^{l_3})| (\mathbf{v}_{32}^{l_2 l_3 l_3'})^* \right) \mathbf{u}_{21}^{l_1 l_2 l_2'}.$$

In both cases the sum over group three can be performed, resulting in summary quantities that play the role of multipole expansions. Schematically we have



Given an "active" group, these averaged quantities and quantities associated with its immediate neighbors are all that is needed to compute the wavefunction for that active group. The derivation of these quantities and their use is complete (for simple cases), and we have begun the implementation of relevant algorithms.

5.3. **Interelectron-cusps.** We note that the representation (5.5) does not account for the inter-electron cusp (see e.g.[47, 43, 38, 44, 45, 37]). As with CI methods, we may still be able to achieve small error in the energy difference of two configurations, which is often the quantity of interest in Chemistry. To achieve high accurary in the wavefunction we are developing an extension to (5.5) that incorporates the cusp.

We consider wavefunctions represented in the form

$$\psi \approx \sum_{p=0}^{P} \left[\left(\sum_{i \neq j} w_p(\|\mathbf{r}_i - \mathbf{r}_j\|) \right) \left(\sum_{l=1}^{r_p} \prod_{k=1}^{N} \phi_j^{lp}(\mathbf{r}) \right) \right]$$

and have developed many of the algorithms needed to use them. The algorithms needed are quite complex, however, so we are deferring their development.

The size-consistent algorithms will eventually need to incorporate the effect of cusps as well, so that we can achieve high-accuracy and size-consistency at the same time.

6. Papers in preparation

As we have obtained a large number of new results, we have several papers in preparation. We list them here.

- Tentative title: "Multiresolution separated representations of lattice sums", G. Beylkin, L. Monzón and R. Harrison.
  (Multiresolution separated representations of Green's functions satisfying boundary conditions and associated fast algorithms).
- Tentative title: "Separated representations of lattice sums for oscillatory Green's functions", G. Beylkin, L. Monzón and R. Harrison.
  (Separated representations for oscillatory Green's functions).
- Tentative title: "Approximation of multiparticle Green's functions via separated expansions", G. Beylkin, M. Mohlenkamp, L. Monzón and F. Pérez
  (A novel approach and algorithms for constructing accurate approximations for multiparticle Green's functions (for energies below scattering states) using expansions via Gaussians)
- Tentative title: "Multiparticle bound states of Bose-Einstein Condensate", G. Beylkin, M. Mohlenkamp, L. Monzón and F. Pérez
  (A constructive approach to computing multiparticle bound states for confining quantum harmonic potential).
- Tentative title: "On approximation of multi-variable functions by exponential sums", G. Beylkin and L. Monzón
  (A nonlinear approximation of functions of several variables via linear combination of exponentials, an important extension of [14]).
- Tentative title: "Approximating a wavefunction as an unconstrained sum of Slater determinants", G. Beylkin, M. Mohlenkamp and F. Pérez
  (Methodology for using [11] for quantum-mechanical systems and basic tests of its efficiency and accuracy.)
- Tentative title: "A center-of-mass principle and algorithmic size-consistency for the multiparticle Schrödinger equation", G. Beylkin and M. Mohlenkamp
  (Structures and algorithms for size-consistency, and the multipole-like expansions that they reveal.)
- Tentative title: "Capturing the interparticle cusp in the multiparticle Schrödinger equation", G. Beylkin and M. Mohlenkamp
  (Structures and algorithms for simultaneously capturing the cusps between all pairs of electrons.)

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